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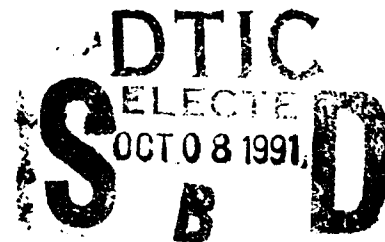
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IONIZATION AND NEUTRALIZATION PROCESSES

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24 May 1991



Final Report
1 April 1988-31 March 1991

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91-12553



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REPORT DOCUMENTATION PAGE

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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 24 May 1991		3. REPORT TYPE AND DATES COVERED Final Report (1 Apr 1988-31 Mar 1991)	
4. TITLE AND SUBTITLE Ionization and Neutralization Processes				5. FUNDING NUMBERS PE 61102F PR 2303 TA G2 WU AI Contract AFOSR-88-0190	
6. AUTHOR(S) David R. Bates					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Queen's University of Belfast Dept of Applied Mathematics and Theoretical Physics Belfast BT7 1NN, NORTHERN IRELAND				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Phillips Laboratory Hanscom AFB, Massachusetts 01731-5000 Contract Manager: Edmund Murad/PHK				10. SPONSORING/MONITORING AGENCY REPORT NUMBER PL-TR-91-2203	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A review on dissociative recombination between positive ions and negative ions of polycyclic aromatic hydrocarbons has been published. Accurate R-matrix calculations of dielectronic recombination of O^+ have been made. A new recombination process, tidal termolecular ionic recombination, has been discovered. Termolecular association between diatomic ions and diatomic molecules has been discussed. Rate coefficients for excitation and charge transfer in $N-O$, $N-O^+$, N^+-O collisions have been calculated. Transition probabilities have been computed for several bands of O_2 . The production of $O(^1S)$ from the dissociative recombination of O_2^+ , and the production of vibrationally excited O_2^+ in the nocturnal F-region, have been considered. Regarding the formation of heavy O_3 and heavy CO_2 , a proof has been given that isotopic fractionation cannot be explained by symmetry considerations alone, and it has been argued that the enhancement of heavy O_3 observed in the stratosphere is due to termolecular association. A review on negative ions has been written. Cross sections for photoionization of $O(2p^4\ 3p, 1D, 1S)$, $O(2p^3 3s, 3,5S^o)$, $O(2p^3 3s\ 3,5P^o)$ and $N(2p^3\ 4S^o)$ have been calculated by the R-matrix method. R-matrix calculations of electronic excitation of N_2 by electron impact agree well with experiment for the $X \rightarrow A$ and $X \rightarrow W$ transitions and reveal the importance of resonances.					
14. SUBJECT TERMS Dissociative recombination Dielectronic recombination Termolecular ionic recombination Radiative & termolecular association		Atmospheric collision processes O_2 bands $O(^1S)$ production F-region Negative ions		15. NUMBER OF PAGES 20	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		16. PRICE CODE	
		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified		20. LIMITATION OF ABSTRACT SAR	

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A more extensive calculation for $e-N_2$ is underway. Also, preliminary studies of electronic excitation in $e-O_2$ collisions indicate reasonable agreement with experiment.

CONT OF BLOCK 14:

Heavy O_3 and heavy CO_2 formation

Photoionization

Electron-molecule collisions

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A. Dissociative recombination

A review article on dissociative recombination and recombination between positive ions and negative ions of polycyclic aromatic hydrocarbons has been published (D.R. Bates and E. Herbst in Rate Coefficients in Astrophysics Eds. T.J Millar and D.A. Williams p. 45, Kluwer Academic Publ 1988).

The key question in the context of the dissociative recombination of polyatomic ions is: What are the dissociation products? One of the factors which controls this is the occurrence of favourable crossing of potentials. It is not possible to determine theoretically whether or not there is a favourable crossing without doing very lengthy ab initio quantal computations but some relevant elementary considerations have been discovered. There are two main classes of saturated polyatomic ion. A member of the first class has a free valence or contains an ionized atom (for example C^+) the number of whose valences increases on neutralization. Breaking a bond yields radicals, and generally there are enough accessible potentials to make a crossing quite likely. A member of the second class contains an ionized atom (for example N^+ or O^+) the number of whose valences decreases on neutralization so that one of the products of breaking a bond is a saturated molecule and only a single potential is accessible (D.R. Bates, Astrophys. J. 344, 531, 1989). Branching ratios cannot easily be predicted. Each depends on the favorability of the crossing (as measured by the Franck Condon factor) and the probability of the radiationless transition. The badly needed guidance from experiment has recently been provided which should enable the theory to be developed. Work on this has been begun.

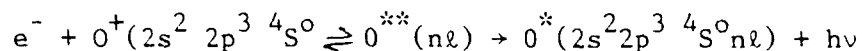
Because of some apparent evidence that the recombination coefficient falls off more sharply than as $T^{-\frac{1}{2}}$ Bardsley (J. Phys B: Atomic and Mol Phys 1, 365, 1967) introduced indirect dissociative recombination.

This involves a sequence of two radiationless transitions, the first into a Rydberg state in an excited vibrational state, the second into the same repulsive state that makes the direct process possible. It is generally believed that the indirect process is unimportant for diatomic ions but is important for polyatomic ions for which the dissociative recombination coefficient tends to be greater. Detailed computations have not been done but it has been reasoned that the indirect process is favoured by the many vibrational modes of polyatomic ions. However it has been shown (D.R. Bates, J. Phys. B: At Mol. Opt. Phys. 24, 695, 1991) that the indirect process is in fact unimportant compared with direct dissociative recombination because it depends on a break-down of the Born-Oppenheimer approximation and there are consequential restrictions on the changes in the normal vibrational modes of the system.

The recombination coefficient is abnormally high ($> \sim 1 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$) for two groups of ion: the group comprising the heavy inert gas ions and dimer ions like O_2^+ and the group comprising cluster ions like H_3O^+ . The phenomenon is so striking that it is appropriate to introduce the term super-dissociative recombination. It has been shown that in the case of the first group the observed high recombination coefficient stems mainly from dissociative recombination being able to populate many Rydberg levels. Cluster ion recombination is at the opposite extreme. Energy considerations show that the neutral products of the dissociation must be in their ground states. The high recombination coefficient here stems mainly from the radiationless transition involved being of the fast single-electron type. Both types of recombination are facilitated by the potential gradient at the crossing being considerably less than for normal dissociative recombination. (D.R. Bates, J. Phys. B: At. Mol. Opt. Phys. 24, 703, 1991).

B. Dielectronic recombination of O^+ .

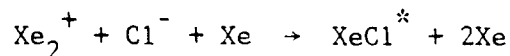
Accurate calculations on the photoionization of atomic oxygen carried out at Queen's University Belfast by Bell et al (1989, J.Phys.B: At.Mol.Opt.Phys. 22, 3197) raised the prospect of obtaining, for the first time, accurate rates for the dielectronic recombination process:



where O^{**} is a resonance state. Hence these earlier eleven-state R-matrix photoionisation calculations were extended to obtain this dielectronic recombination rate. It was found that the rate coefficients are about one-half of those obtained by Badwell and Pindzola (Phys.Rev. A39 1690, 1989) using a less accurate distorted wave method, with a maximum value of $3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at an electron temperature of about 10 eV. This work is described in the forthcoming paper by Terao et al (J.Phys.B:At.Mol.Opt.Phys. submitted, 1991).

C. Tidal termolecular ionic recombination

A new recombination process, tidal termolecular ionic recombination, has been discovered. It arises from calculations aimed at explaining measurements (S.P. Mezyk, R. Cooper and J. Sherwell, J.Phys.Chem. 93, 8187, 1989) on processes like



which were carried out in connection with rare gas halide lasers. The experiments proved that the recombination coefficient is far higher than expected. Monte Carlo simulation that allowed for the $Cl^- - Xe^+$, $Cl^- - Xe$ and $Xe^+ - Xe$ forces showed that the rotational and vibrational modes of Xe_2^+ tend to be excited by the passage of Cl^- through perihelion. Because of this electrostatic tidal action the orbit contracts and the internal energy of Xe_2^+ increases leading to dissociation. The measured values of the recombination coefficient have been reproduced satisfactorily (D.R. Bates and W. Lowell Morgan (Phys.Rev.Lett. 64, 2258 1990).

D. Radiative and termolecular association

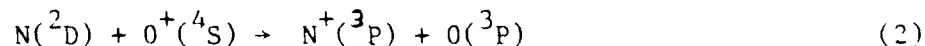
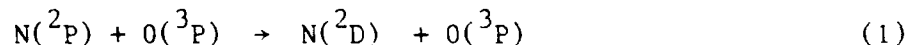
A review article on radiative association has been written (D.R. Bates and E. Herbst in Rate Coefficients in Astrophysics Eds. T.J. Millar and D.A. Williams, p.17 Kluwer Academic Press 1988).

The dependence of the rate coefficient k for termolecular association between the diatomic ions A^+ and diatomic molecules B on the temperature T of the ambient gas has been considered. There is experimental evidence that k decreases rapidly as T is increased if the association energy is small. It was shown that the required T variation could ensue if the reactants in the energized complex AB^{+*} repel one another at some relative orientations (D.R. Bates, J.Chem.Phys. 90, 87, 1989).

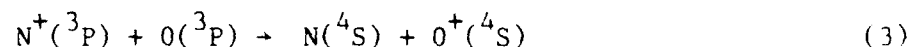
It has been shown that the rate coefficient for the deactivation of $O_2(^5\pi_g)$ by N_2 is probably low enough to ensure that collisional dissociation $O_2(^5\pi_g) + N_2 \rightarrow 2O + N_2$ prevents the reaction $O + O + N_2 \rightarrow O_2(^5\pi_g) + N_2$ from contributing appreciably to the measured total termolecular association coefficient (D.R. Bates, Chem.Phys.Lett. 162, 313, 1989).

E. Some collision processes in upper atmosphere

The Landau-Zener approximation in combination with ab initio NO and NO^+ adiabatic potential energy curves have been used to check the rate coefficients that aeronomers have found appropriate for

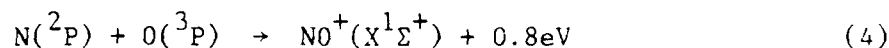


and



The aeronomical results can be rationalized satisfactorily: process (1) and (2) are due to transitions between states of the same species at

avoided crossings of the adiabatic potentials but process (3) is between states of different species brought about by spin-orbit interaction near crossings of the adiabatic potentials. These potentials are not such as to permit the occurrence of the exothermic associative ionization process



that has been accepted in aeronomy. (D.R. Bates, Planet.Space Science 37, 363, 1989).

Theoretical considerations show that if the rate coefficient for $\text{N}(^2\text{D}) + \text{O}(^3\text{P}) \rightarrow \text{N}(^4\text{S}) + \text{O}$ is indeed $2.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ as measured by L.E. Jusinski, G. Black and T.G. Slanger (J.Phys.Chem. 92, 5977, 1988) the product oxygen atoms must be in the ^1D state. This is incompatible with observational data on the forbidden red line emission. It was inferred that the $\text{N}(^2\text{D}) + \text{O}(^3\text{P})$ quenching measurement must have been vitiated by some factor which did not enter a companion $\text{N}(^2\text{D}) + \text{O}_2(\text{X})$ quenching measurement (D.R. Bates, Planet. Space Science 37, 1145, 1989).

F. Transition probabilities for O_2 bands

Absolute transition probabilities have been computed for the bands of the Herzberg I, Chamberlain, Herzberg II and Herzberg III systems of molecular oxygen (D.R. Bates, Planet. Space Science 37, 881, 1989).

G. $\text{O}(^1\text{S})$ production and the nocturnal F-region

The $\text{O}(^1\text{S})$ quantum yield in O_2^+ dissociative recombination $f(^1\text{S})$ in the nocturnal F-region and processes $\text{O}^+ + \text{O}_2 \rightarrow \text{O} + \text{O}_2^+$ ($v \leq 7$) and $\text{O}_2^+(v) + \text{O} \rightarrow \text{O}_2^+(v' < v) + \text{O}$ have been discussed. The values of $f(^1\text{S})$ obtained from the Visible Airglow Experiment (V.J. Abrev, S.C. Solomon, W.E. Sharp and P.B. Hayes, J.Geophys.Res. 88, 4140, 1983) do not seem explicable in terms of the ab initio results of Guberman (Nature, 327,

408, 1987) on the $\alpha(^1S,v)$ direct dissociative recombination coefficients. Arguments have been advanced to show that the discrepancy cannot be attributed to an overlooked $O(^1S)$ source in the F-region. Doubt has been thrown on the correctness of the results of the Visible Airglow Experiment by a recent determination of the $f(^1S)/f(^1D)$ ratio by H. Takahashi, B.R. Clemensha, P.P. Batista, Y. Sahai, M.A. Abdu and P. Muralikrishna (Planet. Space Sci. 38, 547, 1990) from equatorial F-region profile measurements. These are consistent in general with theoretical expectations. However discrepancies appear in detailed facets of the data. If they are real they may conceivably be due to the computed $\alpha(^1S,v)$ being less accurate than has been supposed. The possibility has been raised that $\alpha(^1S,0)$, in particular, is affected by the neglected indirect dissociative recombination. Laboratory measurements on $f(^1S)$ by J.L. Queffelec, B.R. Rowe, F. Vallee, J.C. Gomet and M. Morlais (J.Chem.Phys. 91, 5335, 1989) have been considered and it has been concluded that they conflict with so much independent evidence that they must be regarded with reserve (D.R. Bates, Planet. Space Science 38, 889, 1990).

H. Isotopic fractionation and the formation of heavy ozone and heavy carbon dioxide

Some scientists have believed that the isotopic fractionation that is known to occur in the formation of ozone and carbon dioxide can be explained by symmetry considerations alone. A proof has been given that this is impossible (D.R. Bates, J.Chem.Phys. 93, 2158, 1990).

Specifically breaking termolecular association of ozone into two steps



it has been proved that no isotopic fractionation can ensue if the

energized complex O_3^* is distributed statistically amongst its internal modes. It has been argued (D.R. Bates, J.Chem.Phys. 93, 8739, 1990) that this can only mean that the O_3^* does not have time to attain energy randomization before it dissociates back into the reactants. Let X denote either of the heavy isotopes of oxygen and \sim denote the bond formed in association. Step (2) may then be written



in the case of regular ozone; and may be written

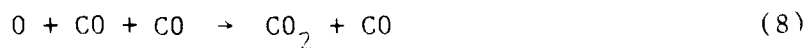


in the case of heavy ozone. Step (3) does not lead to enhancement but the combination of steps (5) and (6) do. Some of the fractionation arising from them may be transferred to the symmetrical isomer by the flip transformations



in which the end atoms move towards one another breaking the original bond and forming a new bond. The measured $[OXO] : [OOX]$ ratio is reproduced if the flip frequency is the same as the dissociation frequency. Calculations have been done on the variation of the enhancement with the ambient gas density. We have reasoned that the enhancement observed in the stratosphere is that due to termolecular association and that the lower values obtained in laboratory experiments are artifacts.

The measured isotopic enrichment of carbon dioxide in other laboratory experiments may arise from termolecular association



from enriched OXO^* that is generated in another association process or from both. The apparent scatter in the results is much greater than would be expected from the precision of the measurements. We have

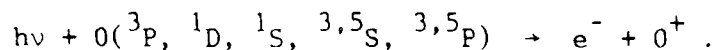
argued that this may be an artifact similar in origin to those for ozone (DR Bates, J.Chem.Phys. 93, 8739, 1990).

I. Negative ions

A long (80 page) review article "Negative ions: structure and spectra" has been written (D.R. Bates, Adv.Atomic.Molec. and Optical Physics, 27, 1990). During the past decade great progress has been made, mainly, but not entirely, due to laser photoelectron spectroscopy to tunable laser photodetachment threshold studies and ab initio quantal calculations. For example, new stable atomic anions have been discovered; some unexpected excited atomic anions have been investigated and found to have interesting properties; the predicted dipole-supported type of excited state have been observed and the spectroscopic constants of many diatomic and polyatomic molecules have been determined with, in a number of instances, very high accuracy. The research that has been done has been summarized with attention focused on the results (i.e. the properties of the anions) rather than the methods used in obtaining them.

J. Photoionization of atomic oxygen

In the work performed, studies have been made for the photoionisation of the $2p^4\ ^3P$, 1D , 1S ; $3s\ ^3,5S^o$ and $3p\ ^3,5P$ states of atomic oxygen



Whilst photoionisation of the $2p^4\ ^3P$ ground state has been investigated theoretically for the last fifty years, limited research has been carried out on the photoionisation of excited states. Indeed for all of the above excited states the theoretical work has been limited to the extent that none of it has included autoionising resonances. An important feature of the present work is therefore the inclusion of such resonances. Despite all of the work on the ground state, there are

still several discrepancies between theory and experiment, particularly above the $4S^0$ threshold and the $2P^0$ threshold. Part of this work therefore has been to improve on the calculations of Pradhan (J.Phys.B:At.Mol.Phys. 11, L729, 1978) and Taylor and Burke (J.Phys.B: At.Mol.Phys. 9, L353, 1976). These authors employed R-matrix approach and includes some 0^+ target states arising from the $2s^2 2p^3$ and $2s 2p^4$ configurations.

In all of the calculations performed in this study, we employed the R-matrix method and included eleven target states of 0^+ : $2s^2 2p^3 4S^0$, $2D^0$, $2P^0$; $2s 2p^4 4P$, $2D$, $2S$, $2P$; $2s^2 2p 3s 4P$, $2P$, $2D$, $2S$. Each of these states was represented by configuration-interaction type wave functions and the energies and energy separation between levels agreed closely with experiment and represented a significant improvement on all previous calculations.

1. $3P$ state

Figure 1 displays the present results. The most significant conclusion is that the theoretical data has converged and thus the discrepancies, above the $4S^0$ and $2P^0$ threshold, with experiment still remain but must almost certainly lie with the experimental procedures. We shall see below the photoionisation cross sections for the $1D$ and $1S$ states are dominated by a broad resonance, the position of which lies in the region above the $2P^0$ threshold. A possible explanation therefore of the discrepancy above the $2P^0$ threshold is that there may exist excited states of atomic oxygen in the experimental beam. However, we note that this is not applicable to experiment of Hussein et al (J. Phys. B: At. Mol. Phys. 18, 2827, 1985).

2. $1D$, $1S$ states

Figures 2 and 3 display the present results. The wide divergence among previous results is clearly apparent. The significant discovery of

the present study is the occurrence of a broad $2s2p^5\ ^1P^o$ Coster-Kronig resonance in both the 1D and 1S state photoionisation cross sections.

3. $3s\ ^{3,5}S^o$ and $3p\ ^{3,5}P$ states

The only theoretical work available for these states is that of Saxon et al (Phys. Rev. A39, 1156, 1989) for the $3p\ ^3P$ state. Their work did reveal the interesting feature of a Cooper minimum in the $O^+(^4S^o)\epsilon\ ^3D^o$ final channel, but did not include allowance for autoionising resonances. Thus, the present work is not only the sole data available for the $3s\ ^{3,5}S^o$ and $3p\ ^5P$ states (very limited experimental data exists) but is the most sophisticated for all states. Cooper minima were found for both the $3p\ ^3P$ and $3p\ ^5P$ states and careful analysis using oscillator strengths for neutral oxygen was performed to confirm both the accuracy of the present calculation and hence the position of the Cooper minima. For the $2p^33s\ ^{3,5}S^o$ states it was found that the photoionisation cross sections are dominated at high energies by the contributions arising from ejection of a 2p electron (the 3s behaving like a 'spectator' electron).

The above work is described in two papers (K.L. Bell et al, J Phys B: At.Mol.Opt.Phys. 22, 3197, 1989 and K L. Bell et al J.Phys.B:At.Mol.Opt. Phys. 23, 2259S, 1990).

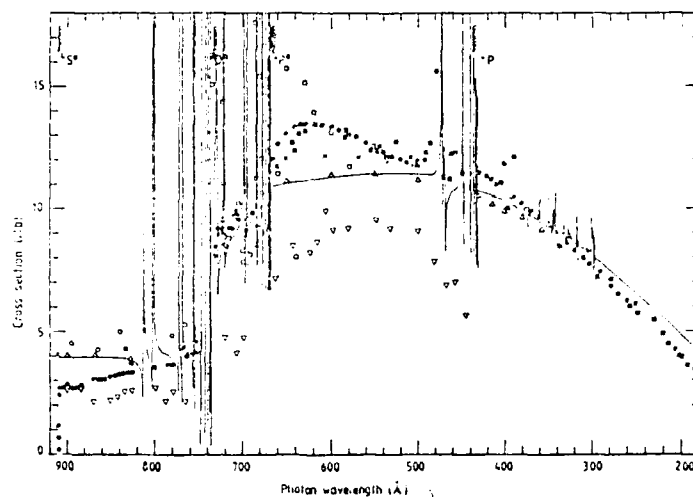


Figure 1. Photoionisation cross section of the 3P state of atomic oxygen. Theory: —, present results, Δ , Pradhan (1978); \times , Taylor and Burke (1976). Experiment: ∇ , Coines *et al* (1968); \circ , Kohl *et al* (1978); \square , Hussein *et al* (1985); \blacksquare , Samson and Pareek (1985); \odot , Angel and Samson (1988). (Thresholds correspond to experimental values.)

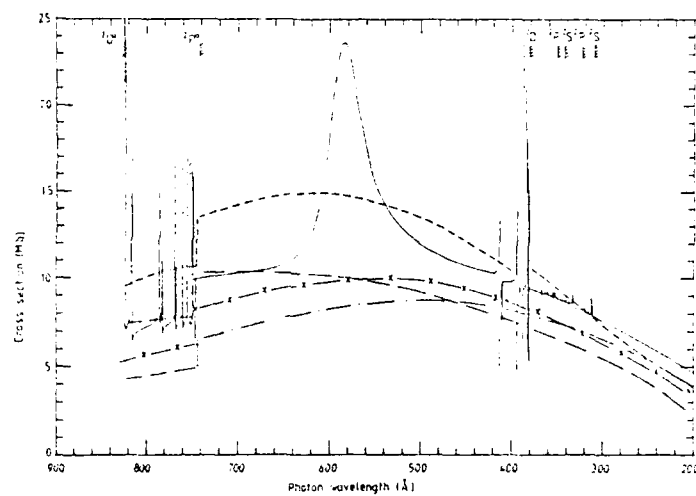


Figure 2. Photoionisation cross section of the 1D state of atomic oxygen. —, present results, - - - (length), — (velocity), Henry (1967), - x -, Thomas and Hellawell (1970), - - -, Koppell (1971). (Thresholds correspond to experimental values.)

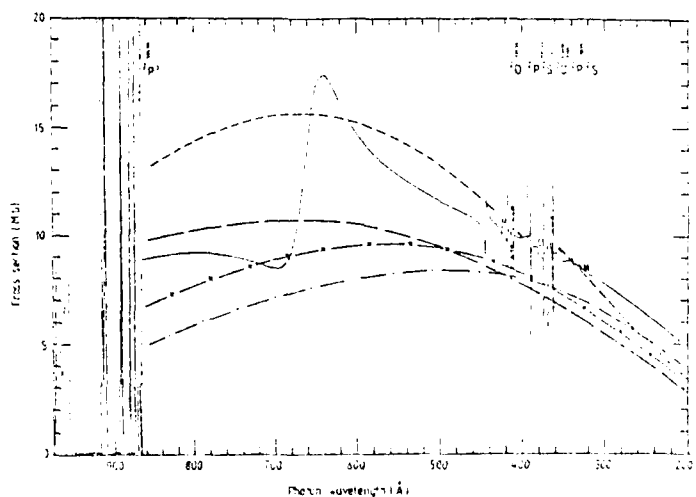


Figure 3. Photoionisation cross section of the 1S state of atomic oxygen. —, present results, - - - (length), — (velocity), Henry (1967), - x -, Thomas and Hellawell (1970), - - -, Koppell (1971). (Thresholds correspond to experimental values.)

K. Photoionization of atomic nitrogen

A study of the photoionisation of the ground $4S^0$ state of atomic nitrogen has been carried out. The R-matrix method was used and nine target states of N^+ have been included in the calculation: $2s^2 2p^2 \ ^3P$; $2s2p^3 \ ^5S^0$, $^3D^0$, $^3P^0$, $^3S^0$; $2s^2 2p3s \ ^3P^0$; $2s^2 2p3p$, 3D , 3S , 3P . The results are found to differ little from the less sophisticated work of Le Dourneuf et al (J. Phys. B: At. Mol. Phys. 12, 2449, 1979). This is significant in that it demonstrates that the R-matrix calculations have converged and that the cross section is known now to an accuracy of better than a few per cent. The results also provided an explanation of the discrepancy between theory and experiment which had previously existed. This work is described in a paper by K L. Bell and K A. Berrington (J Phys B:At Mol.Opt.Phys. 24, 933, 1991).

L. Electron-molecule collisions

For collisions between electrons and diatomic molecules, many calculations have been reported on vibrational and rotational excitation in which the electronic state remains in the ground state throughout. At Queen's University Belfast, the R-matrix method, whose original application in atomic physics was to continuum processes involving single atoms or ions, was extended to electron-molecule collisions, and accurate cross sections were obtained for roto-vibrational excitation of molecules such as N_2 , HF and HCl in their ground electronic states.

Regarding electronic excitation of molecules by electron impact, the R-matrix method was applied to the excitation of H_2 to the $b \ ^3\Sigma_u^+$ state, and gave results that agreed well with calculations using the linear-algebraic-equations method and the Schwinger variational method. However, apart from H_2 , there has been little reliable work on electronic excitation in electron-molecule collisions, even though such

processes, for molecules such as N_2 and O_2 , are important in many physical situations.

Against this background, a program of work has been undertaken at Queen's University Belfast, with the support by the U.S. Airforce and in collaboration with the Daresbury Laboratory, to calculate accurate electronic-excitation cross sections for N_2 and O_2 using the R-matrix method. For the first time in electron-molecule collisions, configuration-interaction wavefunctions have been used to represent the electronic states of the target molecule, this being important in order to obtain accurate energy-spacings and transition-moments.

For N_2 , attention has initially been focused on transitions from $X \ ^1\Sigma_g^+$ ground state to the first three low-lying valence excited states $A \ ^3\Sigma_u^+$, $B \ ^3\Pi_g$ and $W \ ^3\Delta_u$. The results, described in a paper by CJ Gillan, CJ Noble and PG Burke (1990), show that these cross sections are dominated by resonances over the first 10eV. Good agreement was obtained with experiment for the $X \rightarrow A$ and $X \rightarrow W$ transitions, but this work indicated the need to include more target states and to include the effects of nuclear motion which had been neglected in these preliminary calculations. Presently, a more accurate calculation involving eight valence excited target states is nearing completion.

Work is also well underway on $e-O_2$ collisions. Nine target states, arising from the configurations $1\pi_u^4 1\pi_g^2$ and $1\pi_u^3 1\pi_g^3$ are being included in the calculation. Of prime interest is the transition from the $X \ ^3\Sigma_g^-$ ground state to the first two electronically excited states $a \ ^1\Delta_g$ and $b \ ^1\Sigma_g^+$. This work, which will be submitted for publication soon, yields results that are in reasonable agreement with experiment.

Data from these calculations is being further analysed to yield differential cross sections for both free and oriented molecules. A similar analysis will also be applied to the e-N₂ results.

LIST OF PUBLICATIONS GENERATED UNDER GRANT

1. Theoretical considerations regarding some inelastic atomic collision processes of interest in aeronomy: deactivation and charge transfer.
Planet. Space Sci. 37, 363 (1989)
by D.R. Bates.
2. Oxygen band system transition arrays.
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